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Membrane gas separation – physical solvent absorption combined plant simulations for pre-combustion capture

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Abstract

Removal of carbon dioxide (CO_2) from syngas generated by coal gasification is often currently achieved by absorption into physical solvents such as in the Rectisol Process. The vented gas from this process often does not have the CO_2 purity required for carbon capture and storage purposes, because the focus is on recovery and recycling valuable syngas components, such as H_2. It is shown here that this can be rectified through the use of a CO_2-selective membrane. For an existing Rectisol process, a CO_2-selective membrane unit on the vented waste gas can achieve the necessary CO_2 purity with a low CO_2/H_2 selectivity polymer. This provides a simple and effective method to retrofit such a process to provide a CO_2 stream suitable for storage. Alternatively, the standard multiple flash stages can be replaced by a single flash stage with a gas-separation membrane on the gas recycle. This Rectisol – membrane hybrid design can achieve high purity CO_2 product streams with reasonable membrane CO_2/H_2 selectivities, dependent on the solvent flash pressure. However, maximizing CO_2 flux across the membrane means a high flashing pressure and therefore only partial solvent regeneration before recycle to the absorber. This results in a significant increase in solvent flowrate and hence absorber size to ensure high CO_2 recovery.

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Keywords: Pre-combustion; Physical solvent; Membrane gas separation; hybrid process

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1. Introduction

Emissions of carbon dioxide from fossil fuels and resulting anthropogenic climate change are significant environmental and economic issues. Carbon capture and storage (CCS) is a proposed strategy to reduce carbon emissions from coal-fired power stations, and involves three possible strategies: post-combustion, oxy-fuel combustion and pre-combustion [1]. The focus here is on pre-combustion capture, involving the gasification of coal into syngas and the subsequent separation of CO_2 before the syngas undergoes combustion or is used as a feedstock material for chemical processing. Pre-combustion can be further classified into oxygen or air-blown gasification, the latter producing a syngas with a significant nitrogen content [2].

Commercially, CO_2 separation from syngas is often undertaken using physical absorption solvents [3, 4]. These utilize the high pressures of the syngas to achieve strong absorption into solvents that have a high solubility for CO_2 (and H_2S). These solvents are predominately weak Lewis bases, and commercialized under the trademark names of Rectisol (methanol), Selexol (dimethyl ether of polyethylene glycol) and Purisol (n-methyl-2-pyrrolidone) [3]. The CO_2 loaded solvent is subsequently regenerated by being flashed through a number of stages, resulting in desorption of CO_2 because of reduced solubility at the lower partial pressure. Thermal regeneration or inert gas purging is also common to reduce the CO_2 loading in the physical solvent, especially if H_2S is present [3]. The lean solvent is then repressurized and recycled back to the absorber. The advantages of physical solvents are their ability to recover almost all CO_2 from the syngas, and their chemical resistance to degradation from other syngas components. However, physical solvents have difficulty in producing a CO_2 product stream of sufficient purity for storage, > 95 % [1]. This is due to the sorption of other syngas components, such as H_2, CO and N_2, in the solvent at pressure. Flash regeneration results in these gases being released along with the CO_2, diluting the CO_2 concentration in the exit gas. To minimize losses of H_2 and CO, the off-gas from the first flash process is generally recycled back to the absorber, with only the off-gas from later flash stages vented. The CO_2 concentration in these exit gases is related to the pressure differential between the different flash stages, because of the different partial pressures of the other syngas components. As most of the commercial physical solvent absorptions are employed in the removal of CO_2 from syngas for use in synthetic chemical processes, the CO_2 purity is currently not a significant concern. The recovery of valuable H_2 and CO is the focus. However, with carbon emissions increasingly being regulated worldwide [5], it will become necessary to modify physical absorption processes to ensure a high purity CO_2 product stream is produced for subsequent storage.

Membrane gas separation is based on a semi-selective film that allows one or more gases to pass through at the expense of other syngas components [6]. This enables CO_2 to be concentrated on one side of the membrane. The advantage of membrane technology is the smaller footprint and ease of operation compared to traditional solvent absorption. Importantly, the membrane relies on a pressure driving force across the membrane to achieve separation, which is advantageous for syngas based processes. Here, a physical solvent absorption process based on Rectisol is combined with a membrane gas separation process in a hybrid plant. These process simulations are applied to an oxygen-blown gasification scenario. The process flow diagrams of a standard Rectisol plant for syngas processing is shown in Figure 1. A pre-wash of the feed gas with methanol is used to remove H_2S, heavy hydrocarbons and dehydrate the syngas [7]. This eliminates the need for any thermal regeneration of the solvent.

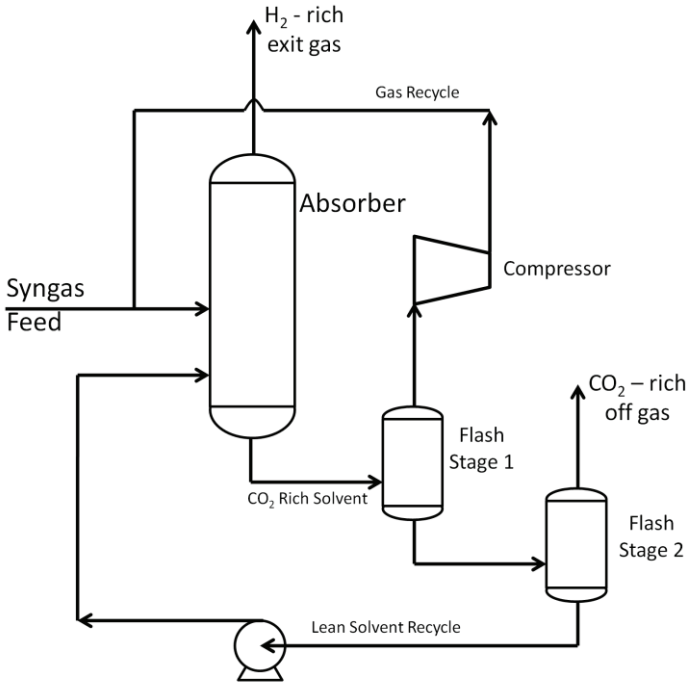

Fig. 1. Process flow diagram of the simplified Rectisol Process simulated here.

2. Simulation Method

All simulations were undertaken using the Aspen HYSYS software package, Version 7.1, with the Peng-Robinson fluid package (AspenTech, USA). The solvent process operations were based on existing units in the HYSYS software package utilizing the modified HYSIM method with adaptive damping to assist in calculation convergence [8]. Rectisol was modelled as pure methanol [7]. The membrane process incorporated a module developed in house specifically for gas separation processes, based on mass transfer equations for cross-flow and counter-flow configurations [9]. The membrane process is broken up into 100 discrete equal stages, where the mass balance is determined iteratively for each stage.

The process was specified to produce a purity of at least 95 % CO_2 and for the entire hybrid process to capture 90 % of the CO_2 in the feed stream [1]. The absorber is designed to operate at the feed syngas pressure to maximize absorption. Subsequent flash stages operate at discrete stages of decreasing pressure, with the final flash stage of the Rectisol only process at atmospheric pressure. The off-gas from the first flash stage is always recycled back to the absorber to maximize the purity of CO_2 produced by later flash stages. For the Rectisol – membrane hybrid plant, the membrane stage is located on the exit gas after the second flash unit to increase the purity or after the first flash stage in the gas recycle loop. The membrane thickness is set at 0.1 μm and a pressure drop of 10 kPa is assumed on the retentate side, with

the permeate stream at atmospheric pressure to maximize pressure driving force across the membrane. The membrane module is operated in a cross flow arrangement with no sweep gas applied.

In the Aspen HYSYS models, all units where operated with their default parameters, with pressure drop in piping negligible, temperature loses negligible and pumps and compressors operating at 75 % efficiency.

The pre-combustion syngas flowrate and the post-wash composition is provided in Table 1, based on an oxygen-blown gasification combined cycle process [2]. The CO_2/H_2 selectivity of the membrane is varied while the H_2O/CO_2 selectivity was set at 100 and the CO_2/CO selectivity is 10 times the CO_2/H_2 selectivity, based on literature reported selectivities [10].

Table 1. Feed conditions and compositions of syngas generated by an oxygen-blown gasification process. These conditions are determined downstream of a methanol wash step.

Feed Conditions	
Mass flowrate (tonnes/hr)	642.4
Temperature (^oC)	130
Pressure (kPa)	2600
mol Fraction	
CO_2	0.402
H_2	0.550
H_2O	0.019
CO	0.029

3. Results and Discussion

For the Rectisol only process, the composition of the gas streams from both flash stages is a function of the pressure of the first flash stage, given that the second flash stage is operated at atmospheric pressure. The CO_2 mole fraction in the recycled gas and CO_2 rich off-gas are shown in Figure 2 as a function of the pressure in the first flash unit. The off-gas always has a CO_2 mole fraction greater than 0.85, and approaches 1 as the operating pressure of the first flash stage decreases. This high purity is because the majority of H_2 and CO sorbed in the solvent are removed in the first flash stage [7]. To achieve a CO_2 mole fraction of more than 0.95 necessary for storage, the first flash stage must be operated at a pressure of 800 kPaa or less. However, operating at a low pressure in the first stage flash unit results in a high gas recycle flowrate, as a large amount of CO_2 is recycled back into the absorber. This can be seen by the CO_2 mole fraction of the recycle gas increasing with decreasing flash pressure (Figure 2).

The large gas recycle flowrate results in a significant re-compression duty, necessary to return the gases to the absorber and minimize H_2 and CO losses (Figure 3). The solvent pump energy duty is negligible compared to the compressor duty except when the pressure of the first flash stage is high.

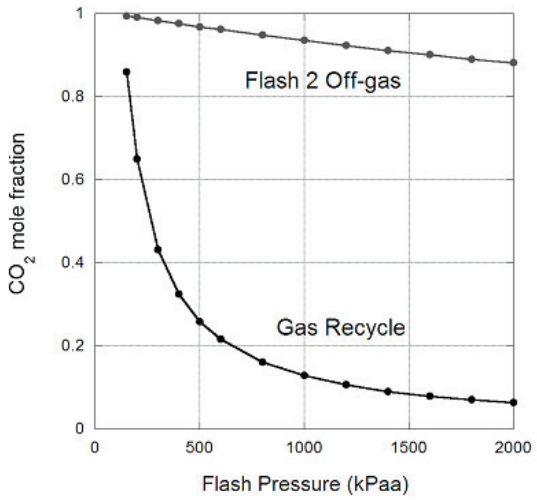

Fig. 2. Rectisol only process base case with O_2-blown gasification, CO_2 mole fraction in the gas recycle stream and Flash stage 2 off gas.

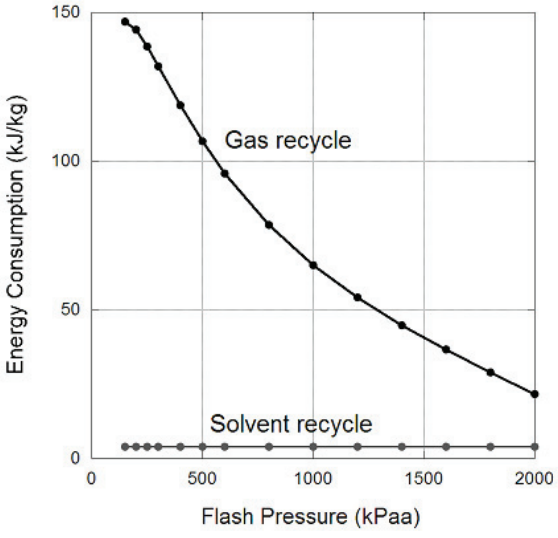

Fig. 3. Energy demand (kJ/kg) of solvent recycle pump and gas recycle compressor as a function of Flash Unit 1 pressure (kPa) for the Rectisol process only.

Greater CO_2 purity in the off gas can be achieved by using a CO_2-selective membrane unit to process this gas (Figure 4). For the Rectisol only process the membrane requires a CO_2/H_2 selectivity of at least 4 to achieve the necessary purity, which is readily achieved with existing rubbery polymeric membranes such as PDMS [11]. Hence, the Rectisol process can be modified with membranes downstream for carbon capture and storage purposes. The required membrane area as a function of CO_2 permeability is shown in Figure 5. For a CO_2-selective membrane such as the highly permeable PDMS [12], the required membrane area is small at about 7000 m^2, while for a less permeable membrane such as PEBAX [13], the required membrane area is 7 x 10^4 m^2, which is a similar size to membrane plants installed for natural gas sweetening [7]. Hence, the required membrane footprint is small, which is beneficial when retrofitting existing plants.

The increased energy demand of the process is associated with the driving force across the membrane. Similar to other membrane processes, the energy duty is minimized by having a vacuum on the permeate stream, rather than a compressor on the feed [14]. The relative increase in energy duty of this process compared to the standard Rectisol process is provided in Figure 6. Over a range of CO_2/H_2 selectivities, the vacuum pump adds an additional 17.8 to 19% energy demand to the process. The waste gas leaving in the membrane retentate stream is rich in H_2 (mole fraction of 0.33 or greater dependent on first flash stage pressure). Undertaking combined cycle power generation with this waste gas stream, to minimise the H_2 loss, could provide at least 45% of the energy needs of the vacuum pump. Alternatively, this waste gas could be compressed and recycled back into the Rectisol process to recover the H_2, which will obviously alter the sizing and composition of the process.

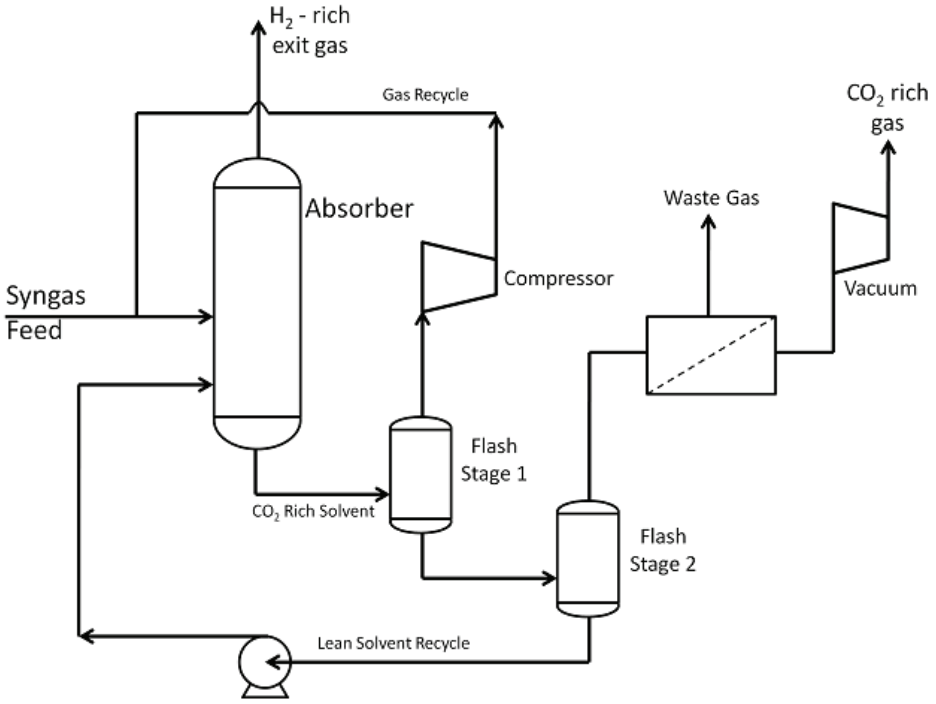

Fig. 4. Process flow diagram of the Rectisol Process with CO_2-selective membrane downstream to ensure CO_2 purity > 95%.

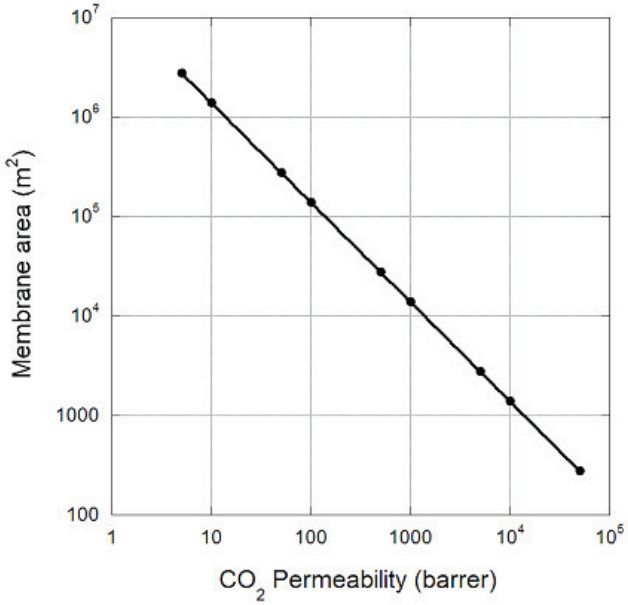

Fig. 5. Relationship between the CO_2 permeability (Barrer) and membrane area (m^2) for a membrane stage with CO_2/H_2 selectivity of 5 on the CO_2 rich off gas.

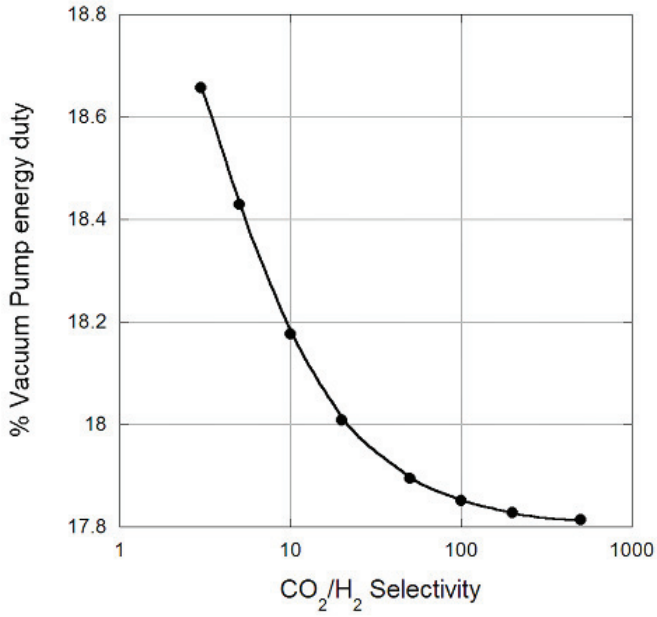

Fig. 6. Vacuum pump energy duty relative to the standard Rectisol process for different CO_2/H_2 selectivity, and a first flash stage pressure of 1200 kPaa.

A membrane may also be incorporated into the Rectisol process to separate CO_2 from the gas recycle stream coming from the first flash stage, Figure 7. The high purity CO_2 product is generated in the permeate stream, with the retentate gas recycled back to the absorber. Placing a CO_2-selective gas separation membrane in this position enables a high CO_2 purity permeate stream, and removes the need for a second flash stage. Important for membrane operation is the feed pressure, which is dictated by the pressure in the flash stage. The pressure of the flash stage also influences the CO_2 mole fraction of the feed gas to the membrane process, shown in Figure 8. As the flash unit pressure is decreased the CO_2 mole fraction in the membrane feed gas increases because more CO_2 is desorbed from the solvent relative to other gases present.

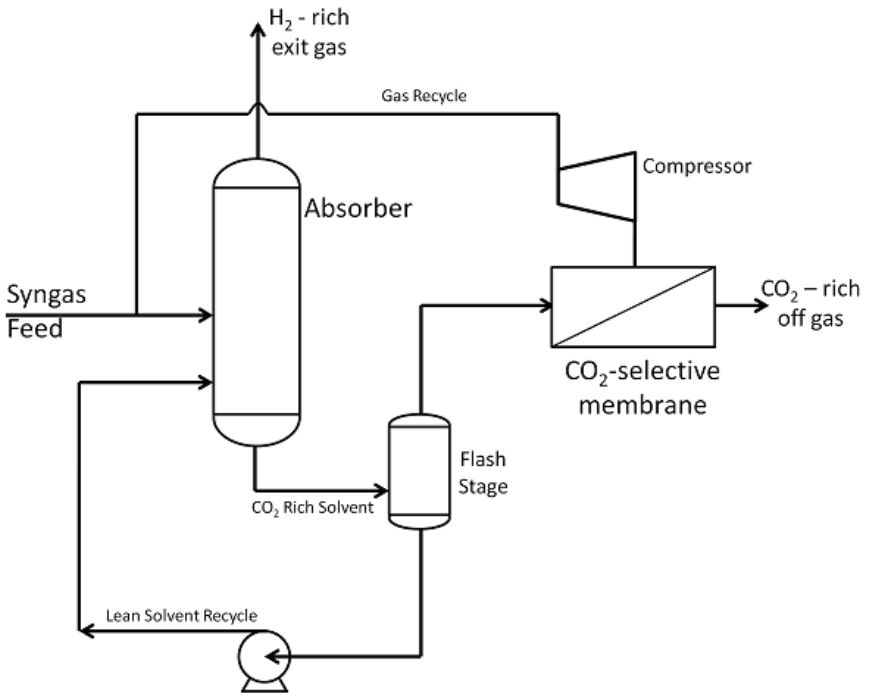

Fig. 7. Process flow diagram of the Rectisol Process with CO_2-selective membrane separating CO_2 from the gas recycle stream..

Operating with only one flash stage results in the solvent not being fully regenerated, and hence retains a significant CO_2 loading. This reduces the performance of the absorber, and to overcome this solvent flowrate must be increased to ensure the absorber captures 90% of the CO_2 in the syngas feed. As a consequence, the absorber diameter for the process configuration in Figure 7 is 2 – 2.8 times larger than the Rectisol only process (shown in Figure 1) to accommodate the extra solvent. This diameter is dependent on the pressure of the flash stage, as it impacts on the CO_2 loading of the solvent recycle. In addition, the required membrane area for this process design is on the order of 1 km^2, which is significantly larger than the membrane area required for retrofitting case above.

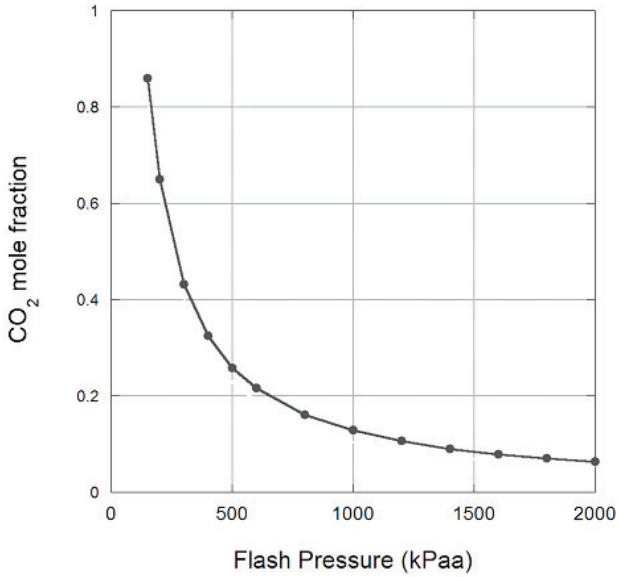

Fig. 8. CO_2 mole fraction in the gas stream leaving the flash stage in the Figure 7 process as a function of the flashing pressure (kPaa).

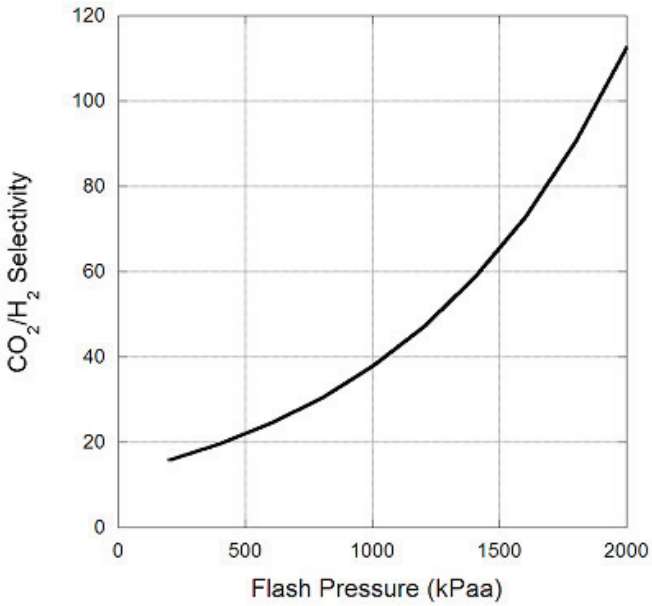

Fig. 9. CO_2/H_2 selectivity necessary to achieve 95% CO_2 purity in the permeate stream as a function of Flash stage pressure (kPaa) for Fig. 7 process (CO_2/N_2 selectivity = 5x CO_2/H_2 selectivity).

The performance of the CO_2-selective membrane depends upon its CO_2 permeability, CO_2/H_2 selectivity as well as the processing conditions. The necessary CO_2/H_2 selectivity to achieve > 95% purity of CO_2 in the permeate stream is provided in Figure 9. As the flash pressure decreases the CO_2/H_2 selectivity also decreases because the CO_2 concentration in the feed increases and lower selectivity is required to achieve the pure product. Most rubbery polymeric membranes have CO_2/H_2 selectivities less than 10 [11]. For these materials to be implemented in this process, the flash unit must operate at a pressure below 300 kPaa.

4. Conclusion

Physical solvents require at least two flash stages to regenerate the solvent and achieve high CO_2 recovery for storage. Existing physical solvent processes can be readily modified by placing a CO_2-selective membrane unit on the flash stage off-gas to achieve the level of CO_2 purity required for carbon capture and storage purposes. This provides a simple and effective method for achieving the required CO_2 purity. As an alternative, a gas-separation membrane in the gas exiting the first flash unit will also enable a high purity CO_2 product stream to be produced. However, the use of a single flash stage in this configuration leads to a high solvent flowrate as the solvent retains a significant CO_2 loading upon recycle, which impacts absorber sizing. Furthermore, current CO_2-selective membranes do not have the CO_2/H_2 selectivity necessary to achieve the level of purity required except at low flashing pressures.

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